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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF CAESIUM.

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I. INTRODUCTION.

SEVERAL considerations led to the renewed investigation of the atomic weight of caesium. Forming as it does the highest known member of an important and well-marked series, this metal might furnish data for the discovery of the long-sought mathematical relationship between the atomic weights; moreover, its study might also lead to the discovery of a yet higher member filling the supposedly vacant place in the classified system. In case both of these somewhat illusory hopes remained unfulfilled, there would yet be obtained data concerning an important constant of nature whose value possessed previously an undesirably large possible error. Moreover, the highly electropositive nature of caesium and its univalence combined to promise the probability of definite results from several compounds, which might throw light upon the possible variability of atomic weights. All these inducements caused us to accept with alacrity the exceedingly kind offer from Professor Horace L. Wells of a large quantity of very pure caesium material, with a view to determining its atomic weight with precision.

II. Review of Earlier Determinations.

Since the discovery of caesium by Bunsen and Kirchhoff in 1860 only four investigations concerning its atomic weight have been made; two by Bunsen * himself, one by Johnson and Allen, † and one by Godeffroy. ‡

In 1861 Bunsen published the results of his first determination. The material used in this investigation was recovered from 150 tons of water taken from the mineral spring at Durkheim. The amount of caesium obtained from this large quantity of water was only about twelve grams, and the difficulty in purifying so small a portion probably accounts for the inaccuracy of the results. Bunsen purified his material by recrystallizing the chlorplatinate, which is not nearly as soluble as the corresponding rubidium salt. The first value found by Bunsen for the atomic weight of caesium was 132.35, but this number was soon afterwards rejected even by himself, since his salt undoubtedly contained traces of rubidium.

A year later, Johnson and Allen, of the Sheffield Scientific School, New Haven, having discovered a much richer source of caesium, began their work on the atomic weight of this element. From the mineral lepidolite found in Hebron, Maine, which contained about three per cent of caesic oxide, they prepared a mixture of lithic, sodic, potassic, rubidic, and caesic chlorides. On treating this mixture with chlorplatinic acid the rubidium and caesium were thrown down as the corresponding chlorplatinates. To separate the rubidium from the caesium, the chlorides were converted through the carbonates into the bitartrates. The acid tartrate of rubidium being only one-eighth as soluble as the corresponding caesic salt, successive fractional recrystallization left the mother liquor nearly free from rubidium. A portion of the salt thus obtained was treated with chlorplatinic acid in quantity sufficient for complete precipitation, and the caesic chlorplatinate thrown down was washed, and reduced in a stream of hydrogen.

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* Bunsen, Zeit. anal. Chem., **1**, 137 (1862); Pogg. Annal. **119**, 1 (1862).

† Johnson and Allen, Am. Jour. Sci. and Arts (2), **35**, 94.

‡ Godeffroy, Annal. der Chem., **181**, 176 (1876).

For the purpose of finding the atomic weight of caesium, they made four determinations of the amount of chlorine in the chloride prepared as above. Silver nitrate was used to precipitate the chlorine, and the precipitated argentic chloride was collected on filter paper. Their highest result was 133.15 and their lowest 132.89, the average being 133.04, if oxygen is taken as 16.000 and the correction to vacuum is applied.

A few months after the appearance of Johnson and Allen's paper, Bunsen published the results of his second investigation. His method of purification was now not unlike that used by the other investigators, the most important difference consisting in the fact that several recrystallizations of chlorplatinate were made, and each successive product was analyzed. The method of analysis also resembled that of Johnson and Allen. The three final results were 132.949, 133.04, and 132.98, averaging 132.99.

In 1865 Redtenbacher * pointed out that there is a greater difference in solubility between the alums of caesium and rubidium than between the chlorplatinates; that therefore these metals might be separated more completely through the former salts than through the latter. Godeffroy made use of this fact in preparing his pure caesium chloride. When he had obtained caesium alum entirely free from rubidium, the alum was dissolved in hot water and the aluminum precipitated with ammonia. After filtering, the solution was evaporated to dryness in a platinum dish, and heated to drive off ammonic sulphate. The residue was then dissolved in water, and baric chloride was added to precipitate the remaining sulphuric acid. After filtering off the baric sulphate the solution was treated repeatedly with ammonia and ammonic carbonate in order to eliminate the last traces of aluminium and barium. The caesium chloride obtained by this treatment was fused in a platinum dish to drive off any trace of ammonium salts that might have been present. On dissolving this fused mass in water, the solution was found to be alkaline, but the crystals deposited by evaporation were not hygroscopic. Godeffroy weighed the chlorine in this salt as argentic chloride, as usual, obtaining four results, which ranged from 132.50 to 132.71, averaging 132.57.

This low result is probably due to the admixture of sodium salts coming from the utensils employed in the complicated manipulation of the material. The salt used by the earlier experimenters was undoubtedly much purer; their errors probably lay in the analysis, and had the

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* Redtenbacher, Wiener. Acad. Anzeiger f., 1865, 39.

opposite tendency. Either the loss of chlorine from the caesic chloride during its ignition, or the solution of argentic chloride by the water used in washing would tend to increase the apparent atomic weight. Hence one might have expected the atomic weight of caesium to lie between 133.0 and 132.6; probably nearer the former than the latter value. The value usually selected by Clarke and others, 132.9, has been in accord with this conclusion, and the present investigation shows it to have been surprisingly accurate.

III. THE ANALYSIS OF CAESIC CHLORIDE.

(a) *The Preparation of Materials.*

Caesic chloride is a colorless salt, crystallizing in anhydrous cubes which are very soluble in water. The aqueous vapor tension of the saturated solution is somewhat greater than that of the average air of American steam-heated laboratories, hence the crystals are deliquescent only on damp days. The German ascription of deliquescence to the salt is due evidently to the moister conditions prevalent in that country. The addition of alcohol to its solution precipitates much of the dissolved salt; and since it has no great tendency to form an acid chloride in solution, hydrochloric acid also precipitates it. Caesic chloride fuses into a limpid, colorless liquid at about 600°, losing a trace of its chlorine thereby if moisture is present and hydrochloric acid absent. On the other hand, the salt shows no trace of alkalinity after fusion in perfectly dry air, especially if it has been recrystallized from a hydrochloric acid solution. In the latter case, acid must always be present in the microscopic inclusions wherever water is, and the trace of hydrolysis on fusion is effectually prevented. Its properties thus fit it admirably for accurate work.

Wells * has shown that caesium may be separated from rubidium and other alkali metals by making use of the difference in solubilities of their trihalide salts. Of these the dichloriodide ($CsCl_2I$) offers peculiar advantages; for this salt not only is from eight to ten times less soluble than the corresponding rubidium salt, but also will crystallize below 70° in a rhombohedral form, while the other metals give the corresponding salts in the orthorhombic form only. By keeping the temperature below this point, crystals of the caesium salt may be obtained which are not likely to carry down rubidium, because of this helpful heteromorphy.

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* Wells, Am. J. Sci. (3), **43**, 17 (1901); Chem. News, **84**, 2184, Oct 4 (1901).

The recrystallization may be carried out very easily without much decomposition by cooling from moderately dilute hydrochloric acid (sp. gr. 1.06). The crystals should then be dried at room temperature; but after they have become almost dry they can be heated to 75° or 80° without much decomposition. In order to test the efficiency of this method, we experimented upon a mixture of 150 grams of lithium, sodium, potassium, rubidium, and caesium chlorides. From this mixture were obtained, after six recrystallizations as dichloriodide, about eight grams of caesic chloride, spectroscopically free from all the other metals, while only traces of caesium remained in the last few residual mother liquors. The greater part of the caesium used in this research had been prepared by Professor Wells in this way.* To test its purity as regards rubidium, the mother liquor from one recrystallization had been evaporated down to an extremely small bulk by systematic recrystallization, and was finally tested in the spectroscope. Not the slightest trace of rubidium could be detected. In all four successive recrystallizations as dichloriodide were made from about a kilogram of the salt, the crystals being well washed each time, and nothing was used over from any mother liquor. The product, weighing about 280 grams, was received from Professor Wells in this state, and our results show that it had reached a remarkable degree of purity.

To obtain the normal chloride from this pure caesium dichloriodide, the latter was placed in a porcelain crucible, and heated at from 90° to 100° in an electric oven, — a temperature far below the melting point of this salt (about 240° C.). The iodine and extra chlorine are slowly driven off, leaving the chloride beautifully white and very porous.

To eliminate any possible trace of iodine which might remain, one might dissolve the salt in a very small amount of warm water, and precipitate with pure alcohol. A better method, however, seemed to be to precipitate it by saturating the solution with hydrochloric acid. The caesic chloride was therefore transferred to a platinum dish, and dissolved in the least possible amount of warm water; hydrochloric acid gas from pure boiling concentrated aqueous hydrochloric acid was passed into the solution by means of a platinum tube; the mixture was allowed to cool, and the mother liquor was poured off into another platinum basin, the precipitate being washed with a little pure concentrated hydrochloric acid. This salt was again dissolved in water, precipitated, washed as before, and partly dried by suction, in a platinum Gooch crucible. After further drying for some time the salt was ready for use. The portion thus prepared was used as Sample I. As will be seen, the atomic weight of caesium found from this sample was 132.886.

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* The source of this material was pollucite, found at Mt. Mica, Paris, Maine.

A second sample was prepared from the mother liquor of the first by evaporating further in platinum vessels and precipitating, as before, with hydrochloric acid gas. The product thus obtained was again dissolved and again precipitated, and after being washed and dried gave Sample II, which yielded the atomic weight 132.883. It was essentially similar to Sample I, and is classed with it below.

The temperature of the caesic chloride solution containing an excess of hydrochloric acid in contact with platinum, must not be allowed to rise above 60° or 70°, otherwise the platinum will be attacked, and some caesium chlorplatinate precipitated, — a mishap which causes much trouble. This difficulty was probably due to the presence of a residual trace of undecomposed dichloriodide. The careful analyst well knows that platinum, which he is forced to use, forms by no means the inert receptacle which he desires. This fact was apparent more than once during the present research, and it is not impossible that both Samples I and II contained traces of platinum from this source, accounting for the slightly high atomic weight. Subsequently this error was yet more vigilantly guarded against, and the later specimens were as free as possible from platinum.

A third sample of caesic chloride was prepared from a somewhat impure caesium alum. In the first place the sulphuric acid was eliminated by means of baric chloride; the dichloriodide was obtained from the filtrate by adding to it an excess of aqua regia, and subsequently adding somewhat more than the calculated amount of iodine. The trihaloid salt separated out, upon cooling, in beautiful rhombohedral crystals. The iodine used in this preparation had been carefully resublimed. The dichloriodide was recrystallized eight times, no trace of rubidium being found by the spectroscope after the third recrystallization, although the original alum had contained much of this impurity. The normal caesic chloride was prepared from this product by heating in the electric oven at 95° for a much longer time than before, until long after all traces of iodine had disappeared; and great care was taken not to allow the solution of caesic chloride to become at all hot when precipitating this salt with hydrochloric acid gas in the platinum vessel. The atomic weight obtained from this third sample was 132.873. A trace of thallium was found spectroscopically in the extreme mother liquors.*

In the search, which proved fruitless, for an unknown heavier metal like caesium, a fourth sample of material was prepared. Since the insolubility of the dichloriodides seems to increase with the atomic weight of the basic element, the unknown element would probably be found in the extreme fraction of crystals. Hence, the most likely way of concentrating a trace of such an element would be to subject a large quantity of the caesium dichloriodide to systematic recrystallization, until a very small amount of substance remained.

Such a process was carried out, starting with 150 grams of the dichloriodide belonging to the sample used in the first analysis. This was systematically fractioned by crystallization twenty-five times, when only about one gram of the substance remained. The normal chloride was prepared from this, and its spectrum was carefully examined. No difference could be distinguished between the spectrum given by this portion and that given by any of the other preceding samples, or the extreme mother liquor. The last four extreme crops of crystals, averaging twenty-three crystallizations, were now combined, and enough caesium chloride was obtained from these for several analyses. The value of the atomic weight obtained from this fourth sample was 132.878, or about the mean of the preceding values.

This result agrees with the verdict given by the spectroscope, showing that recrystallization has in no way affected the purity of the caesium chloride. It must be concluded from this that the most efficient means known to us at present are not capable of isolating any unknown element from this material; and further, that the occurrence of such an element in the original mineral is unlikely. Wells has independently come to the same conclusion. Having gained considerable experience in the technique of all parts of the determination, it now seemed advisable to make a series of determinations in which the highest possible degree of accuracy would be attained at every step.

To this end a fifth portion of caesium chloride was prepared from the already pure chloriodide of Wells. The method of preparation was identical with that employed before, except that in every step greater care was taken, and in driving off the iodine and extra chlorine the salt was heated for two or three days in the electric oven after all apparent traces of iodine had disappeared.

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* This experience agrees with that of Wells, kindly communicated to us in a private communication. It is not impossible that thallium really represents the recurrence of the alkaline characteristics in the periodic system, modified by conflict of overlapping tendencies belonging to other groups.

This treatment left a salt which gave a perfectly colorless solution when dissolved in a small amount of water. Even the mother liquor that remained after precipitating the chloride with hydrochloric acid gas showed no trace of the yellow color due to platinum or iodine. The salt was precipitated twice successively with hydrochloric acid, each time being washed with a concentrated aqueous solution of the same acid. The analysis of this last sample, as will be seen, was conducted with all known precautions, but yielded, nevertheless, a result 132.877, essentially identical with the last.

Silver. Since the ratio of silver to caesic chloride was to be determined, as well as the ratio of argentic chloride to caesic chloride, the purity of the silver to be used must be unquestioned. The method of obtaining the pure metal was so nearly similar to that previously used in this Laboratory that further detailing is scarcely necessary. During the electrolytic part of the purification it is well to wrap the anode in a washed filter, as the "anode dust" is then prevented from mingling with and possibly contaminating the pure silver. The sparkling crystals were thoroughly washed, and fused on sugar charcoal, before the blow-pipe, and cooled in a reducing flame. The melted globule was clear, and free from any film; after cooling it showed no traces of having contained absorbed oxygen. The button was now scrubbed with pure water and clean sand, and cut into small pieces with a clean steel chisel. These pieces were then digested for a short time with dilute nitric acid and washed with ammonia water, in order to remove any traces of iron. To shield them from injurious gases they were kept under distilled water in a small flask. This silver was used in all the analyses, excepting in Nos. 11, 12, 13, 23, 24, and 25. For these analyses the silver was fused in a vacuum on a boat of lime.*

The hydrochloric and nitric acids used were carefully redistilled, the first and last portions of the distillate being rejected. The nitric acid, of course, showed no trace of opalescence with excess of silver nitrate after suitable dilution.† The phosphoric oxide was resublimed in an oxidizing environment. The water used was redistilled, first with alkaline permanganate, and subsequently with a trace of acid potassic sulphate, using in the second case a pure block-tin condenser, fitted to the neck of a Jena flask. It was kept in Jena flasks, and used as soon after distilling as possible. Portions were always tested with the nephelometer * for the presence of chlorine.

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* For further information concerning the preparation and purity of silver, see Proc. Am. Acad., **29**, 64 (1893); **32**, 62 (1896); **33**, 121 (1897), etc.; Z. anorg. Chem., **6**, 98 (1893); **13**, 90 (1896); **16**, 371 (1897).

† Proc. Am. Acad., **29**, 74 (1893).

(b) *Method of Analysis.*

Having now obtained pure material, it was essential to free the chloride from all traces of moisture without loss of a trace of chlorine.

It was soon found that this condition is assured when the substance is fused in a current of nitrogen and bottled in an atmosphere of dry air. For this purpose the apparatus which has been employed in this Laboratory to such advantage in determining other atomic weights is suitable and convenient, — namely, the "bottling apparatus," devised first for preparing and weighing pure magnesic chloride. † This device enables the substance to be ignited in a boat contained in a tube of the hardest glass or porcelain in the purest of dry nitrogen; and the final transference of the boat to the weighing bottle filled with dry air takes place without an instant's exposure to the outside atmosphere. The platinum boat, which had been freed from superficial iron in other investigations, was boiled in several different portions of nitric acid, and finally hydrochloric acid. Afterwards it was scrubbed with clean round sand, washed, ignited, and cooled in its own weighing bottle. Another weighing bottle, containing an appropriate amount of metal, of the same weight and volume as the first, was used as tare. The platinum boat was now weighed in its bottle, the weighing being done by substitution, and all precautions used in recent work done in this Laboratory were strictly followed. ‡ This weight of tube and boat scarcely changed throughout

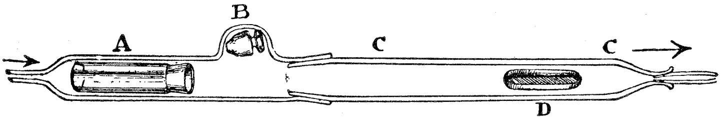

FIGURE 1. — BOTTLING APPARATUS, HORIZONTAL SECTION.
A = weighing bottle. B = stopper of bottle. C C = hard glass tube.
D = Platinum boat containing fused caesic chloride.

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* Richards, Proc. Am. Acad., **30**, 385 (1894); Z. anorg. Chem., **8**, 269 (1894).

† Richards and Parker, These Proceedings, **32**, 55 (1896); Z. anorg. Chem., **13**, 81 (1896).

‡ Richards, Proc. Am. Acad., **26**, 240 (1891); **28**, 1 (1893); **29**, 55; **30**, 369; Z. anorg. Chem., **1**, 150 (1892); **6**, 441 (1893), etc.

the whole series of investigations, and during a single experiment no appreciable variation in weight could be detected.

The boat was now filled with caesic chloride, and placed within the drying apparatus in the position indicated in the diagram, which illustrates the "bottling apparatus," but not the elaborate purifiers of air and nitrogen. The weighing bottle belonging to the platinum boat is placed in the extreme left of the tube A, while its stopper rests in the crevice B, and pure nitrogen thoroughly dried by means of phosphoric oxide was allowed to traverse the apparatus. After about three-quarters of an hour the platinum boat was gradually warmed by means of a large "fish-tail" spreader on the Bunsen burner, so that the whole of the boat may be equally heated. The caesic chloride soon fused, and was kept in a state of tranquil fusion until it was reasonably certain that every trace of residual water must have been expelled. The temperature was now gradually lowered, and the boat was finally allowed to cool to the temperature of the room. A current of air dried by phosphoric oxide was then turned on by opening the appropriate stop-cock, and was allowed to flow for about an hour before the bottling, so as to sweep out all the nitrogen. While the dry air was still flowing, a glass rod was inserted at the right, and the boat was pushed back into its weighing bottle. The stopper was now rolled out of its hiding-place, and was pushed by means of the glass rod firmly into the neck of the weighing bottle. After the tube A had been removed, the weighing bottle was partly removed by means of a hooked wire, and transferred by the aid of a pair of tongs to the desiccator. After suitable delay, the tube, boat, and substance were weighed in the same manner as before.

Since argentic chloride is essentially insoluble in solutions containing either silver or chloride, the chlorine in this pure, dry caesic chloride was precipitated by means of an excess of argentic nitrate. Since, moreover, it was desired to determine the weight of silver needed to effect the precipitation, this argentic nitrate was prepared from a carefully weighed portion of pure silver, and the excess in the filtrate also was weighed as chloride. It is not necessary to describe again the many precautions necessary to carry out, in a strictly quantitative fashion, the solution, mixing, and filtration of these materials, because previous communications from this Laboratory have discussed them in adequate detail. Due care was taken concerning the use of nonactinic light, the collection of the fragments of asbestos often lost from the Gooch crucibles, the traces of water retained by argentic chloride even at 150°, and all the other small causes of error. The most serious cause of difficulty is the dilemma introduced by two conflicting tendencies of argentic chloride, — namely, its solubility and its tendency to absorb argentic nitrate. When it is washed with very dilute argentic nitrate it does not dissolve, but it retains some of the dissolved nitrate; on the other hand, when repeatedly shaken with pure water it retains no impurity, but dissolves to an appreciable extent. In analyses 1 to 10 and 14 to 22, below, the chief precipitate was thoroughly washed by shaking with a solution containing a very small known amount of ionized silver, and the residual liquid moistening the Gooch filter was displaced by a few cubic centimetres of pure water. This reduces each error to a minimum, and almost balances their slight residual effect; but the fused argentic chloride thus obtained is not perfectly white and pearly. Therefore, in the final determinations (11 to 13, and 23 to 25) a safer but more troublesome procedure was adopted. After the precipitate had been well shaken in its glass-stoppered Erlenmeyer flask with several portions of wash water, containing a known amount of silver nitrate, and rinsed with about 50 c.c. of pure water, it was again shaken violently with five separate portions of water (in all about 500 c.c.) which contained no silver nitrate. This treatment was found to remove all traces of adsorbed silver nitrate. These wash waters were kept by themselves, and the amount of dissolved silver chloride which they contained was estimated by means of the nephelometer, this correction being added to the observed weight of silver chloride. Argentic chloride thus washed fuses into a beautiful translucent pearly white mass.

The balance used in this research was the one which has been used in the investigations of many other atomic weights.* It is short armed, and sensitive to about one-fiftieth of a milligram, with the largest load used in this work. The weights were of brass, gold plated. They were very carefully standardized, according to the method suggested by one of us,† and were used in no other work.

All weighings were reduced to the vacuum standard. For this purpose the specific gravity of caesic chloride was determined. 1.0436 and 0.8877 grams of the salt were found to displace, respectively, 0.2313 and 0.1965 gram of benzol at 20°. The specific gravity of the benzol referred to water at 4° was 0.880, hence the two values for caesic chlo-

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* Richards, Proc. Am. Acad., **26**, 242 (1891).

† Richards, Jour. Am. Chem. Soc., **22**, 144; Z. Phys. Chem., **33**, 605 (1900).

THE COMPARISON OF CAESIC AND ARGENTIC CHLORIDE.

Ag = 107.930; Cl = 35.455.

No. of Analysis.	Sample of CsCl.	Weight of CsCl in Vacuum.	Weight of AgCl in Vacuum.	Ratio AgCl : CsCl = 100.000 : x.	Atomic Weight of Caesium.
1	I	3.83054	3.26240	117.415	132.901
2	I	3.95120	3.36532	117.409	132.892
3	I	2.27237	1.93555	117.402	132.882
4	II	3.02935	2.58003	117.415	132.901
5	II	3.19774	2.72382	117.399	132.878
			Average (a) . . .	117.408	132.891
6	III	2.35068	2.00253	117.386	132.858
7	III	2.06245	1.75678	117.399	132.878
8	III	2.56372	2.18358	117.409	132.892
			Average (b) . . .	117.398	132.876
9	IV	2.01881	1.71972	117.392	132.868
10	IV	1.77391	1.51093	117.405	132.886
			Average (c) . . .	117.399	132.877
11	V	3.08160	2.62484	117.401	132.881
12	V	3.13117	2.66720	117.395	132.872
13	V	5.06656	4.31570	117.398	132.876
			Average (d) . . .	117.398	132.876

ride were 3.970 and 3.975. The average, 3.972, agrees sufficiently well with the value 3.992, found by Setterberg.* Therefore, for every gram of caesic chloride, as weighed in air, 0.00016 gram has been added to correct the observed weight.

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* Oefvers. Stockh. Acad. Forh., **39**, No, 6, 23 (1882).

THE COMPARISON OF CAESIC CHLORIDE AND SILVER.

Ag = 107.930; Cl = 35.455.

No. of Analysis.	Sample of CsCl.	Weight of CsCl in Vacuum.	Weight of Silver in Vacuum.	Ratio Ag : CsCl = 100.000 : x.	Atomic Weight of Caesium.
14	I	3.83054	2.45600	155.967	132.880
15	I	3.95120	2.53351	155.958	132.871
16	I	2.27237	1.45686	155.977	132.891
17	II	3.02935	1.94244	155.956	132.868
18	II	3.19774	2.05023	155.970	132.883
			Average (e) . . .	155.966	132.878
19	III	2.35068	1.50720	155.963	132.876
20	III	2.06245	1.32251	155.950	132.862
			Average (f) . . .	155.957	132.869
21	IV	2.01881	1.29434	155.972	132.886
22	IV	1.77391	1.13743	155.958	132.871
			Average (g) . . .	155.965	132.878
23	V	3.08160	1.97590	155.959	132.872
24	V	3.13117	2.00760	155.966	132.879
25	V	5.06656	3.24850	155.966	132.879
			Average (h) . . .	155.964	132.877

(c) *Results of Analysis of Caesic Chloride.*

The eight average values when collated give the following mean value :

From (a)	Analysis	1 to 5	132.891
" (b)	"	6 to 8	132.876
" (c)	"	9, 10	132.877
" (d)	"	11 to 13	132.876
" (e)	"	14 to 18	132.878
" (f)	"	19 to 20	132.869
" (g)	"	21, 22	132.878
" (h)	"	23 to 25	132.877
	Mean value		132.878

The "probable error" of this result, obtained according to the method of least squares, is only about ± 0.001, if each average is counted as a single determination. Of course, however, this "probable error" gives no clew as to the presence or absence of a possible *constant* error. The accuracy of the work and the purity of the silver may be better tested by comparing the weight of silver taken with that of the argentic chloride obtained; thus 22.93252 grams of silver gave 30.46482 grams of chloride, or 75.275 to 100.00; while Stas found the ratio 75.276 to 100.00. This agreement is as close as could be desired; it shows that no weighable trace of iodine remained in the preparations.

The means (d) and (h) represent by far the most careful work, and the six experiments included in them give the average 132.877 (± 0.0007). This seems to be the most trustworthy value of the atomic weight of caesium as obtained by the analysis of the chloride.

IV. The Analysis of Potassic Chloride.

As a further test of the purity of the materials and the accuracy of the method it seemed worth while to make a few similar determinations of the atomic weight of potassium. Since this value is already well known from the accurate work of Stas, the present work upon this element was far less searching than the preceding investigation.

For this purpose pure potassic chloride was prepared as follows. "Chemically pure" potassic chloride was dissolved in pure water, and to this was added a carefully prepared solution of chloroplatinic acid solution. The potassium chlorplatinate was well washed and reduced by ignition. The potassic chloride was dissolved with hot water in a platinum vessel and the solution was allowed to stand for some time in order that any chlorplatinate which had not been reduced might separate out. The solution was then evaporated, and the potassic chloride repeatedly precipitated with hydrochloric acid gas. No better method could be found for eliminating the last traces of chlorplatinate; for since this latter salt yields a dissimilar anion, it is even more soluble in strong hydrochloric acid than in water, while potassic chloride is almost insoluble in concentrated hydrochloric acid. The successive precipitation was repeated long after the last apparent traces of platinum had disappeared, and the last snow white crystals were washed with a little water and thoroughly dried over potash in a desiccator.

THE COMPARISON OF POTASSIC AND ARGENTIC CHLORIDES.

Ag = 107.930; Cl = 35.455.

No. of Analysis.	Weight of KCl in Vacuum.	Weight of AgCl in Vacuum.	Ratio AgCl : KCl = 100.000 : x.	Atomic Weight of Potassium.
			$x =$	
1	2.50019	4.80600	52.022	39.137
2	2.50391	4.81325	52.021	39.136
	Average		52.022	39.137

THE COMPARISON OF POTASSIC CHLORIDE AND SILVER.

No. of Analysis.	Weight of KCl in Vacuum.	Weight of Ag in Vacuum.	Ratio Ag : KCl = 100.000 : x.	Atomic Weight of Potassium.
			$x =$	
1	2.50019	3.61747	69.114	39.140
2	2.50391	3.62283	69.115	39.141
	Average		69.115	39.141
	Mean value of Series I and II . . .			39.139

The method of analysis was precisely similar to that used in the earlier analyses of caesic chloride, and the same sample of silver was used. The only difference worthy of note is in the fact that while drying the potassic chloride for analysis, fusion did not take place at the highest temperature attainable in the hard glass tube; but the salt was finely powdered, and the heating was maintained for a considerable length of time at about 700°, so as to afford as much opportunity as possible for the escape of the last traces of water and hydrochloric acid. Moreover since the mother liquor contained almost as much chlorine as the potassic chloride, weight for weight, the inclusion of a trace would not greatly affect the result.

The results for the potassic chloride are given in the foregoing table. The mean value 39.139 agrees very closely with the value obtained by Stas, whose later experiments with the chloride gave values ranging from 39.142 to 39.15.

Thus the evidence of this work affirms the trustworthiness of the experiments with caesic chloride.

V. The Quantitative Decomposition of Nitrates.

If a process could be devised which involved the use of a different set of apparatus, and another series of salts, any constant error which might possibly have crept into the previous method would probably not appear, and the new results would furnish a severe test of the correctness of the values found from the chlorine determinations. Hence a search was instituted for an entirely new method, involving different manipulation.

It is well known that when silicic oxide is heated with the nitrate of such a metal as caesium, the salt breaks up according to the following reaction: —

$$2CsNO_3 + SiO_2 = Cs_2O\,(SiO_2) + N_2O_5$$

the nitrogen pentoxide decomposing and passing off, leaving the caesic silicate. Therefore, from the loss in weight of a mixture containing a known weight of caesic nitrate and an excess of silica one might compute the atomic weight of caesium. This method, commonly used to determine nitric acid, has never before served for this exact purpose.

A series of preliminary experiments were of course necessary to determine the limit of accuracy attainable.

The silicic dioxide was prepared from a very pure specimen of natural sand. This material was washed several times with boiling water and then digested with hot concentrated sulphuric acid for several days. Subsequently it was again washed with water and covered with boiling aqua regia. It was allowed to stand on the steam bath in this solution for at least a week. Upon washing and drying the product, it was found to be beautifully white, and when heated to a high temperature in the blast lamp, it came almost at once to a constant weight. After powdering very finely in an agate mortar and heating again it was ready for use. Subsequently very pure artificial silica made from alkaline silicate was tried, but its use was abandoned because of the very great difficulty found in expelling every trace of water from it. All the experiments described below were made with the pure powdered quartz sand.

A rough experiment was first made in order that one might see where errors were likely to appear and what special precautions would have to be taken.

A large platinum crucible containing a short platinum spatula was half filled with the silicic dioxide, ignited for a short time, cooled in a desiccator and weighed, using another platinum crucible containing an equal amount of sand as a tare. Some pure powdered potassic nitrate was then added to the silicic dioxide, and the two were thoroughly mixed with the platinum spatula. The whole was again weighed in order to find the weight of nitrate added. Subsequently a large amount of the dioxide was spread over the top until the crucible was three-quarters full, and the whole was weighed again. This layer on top serves to catch any of the nitrate which might otherwise be carried away with the escaping vapors of the oxides of nitrogen. In order to find whether or not any moisture had been taken up during the mixing, the crucible was heated in the electric oven for two hours at about 150° C., cooled in a desiccator and weighed. The loss actually found after this additional drying never amounted to more than 0.00004 of a gram. The last weight was of course taken as the true one.

The mixture was now very carefully heated in the flame of the Bunsen burner, keeping the temperature at a comparatively low point for several hours and gradually increasing the heat until the temperature of the blast lamp was reached.

The melting point of potassic nitrate is about 339° C., while the caesic nitrate melts near 414° C.*; the full heat of a Bunsen burner should bring the silicate to a constant weight in either case.

It was soon noticed that the nitrate had a tendency to creep over the sides of the crucible, when a little above the fusing point. That part of the nitrate next the platinum, not being entirely surrounded by the sand, evidently had not the same opportunity of combining with the silica as the remainder of the salt; the exposure of this nitrate obviously might cause a loss by sublimation at a high temperature.

This danger was eliminated by using a small platinum crucible inside the larger one, in which to mix the nitrate and sand; this small crucible was completely surrounded and covered with a layer of silicic dioxide.

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* This temperature was found in a capillary hard-glass tube by means of a nitrogen-filled mercury thermometer, using a bath of potassic nitrate. The thermometer was suitably standardized and corrected for the cool column.

If with this arrangement the heating is conducted slowly and cautiously, no evidence appeared of loss by sublimation. No trace of deposition was found upon the under surface of the clean cool platinum lid of the crucible.

Potassic and caesic silicate both seem to be essentially permanent and non-volatile at 1000°, as far as the present experiments were concerned, and constant weight was easily reached.

The next problem to be solved was the finding of the best source of heat. In the first place, in order to avoid the danger of contamination from the impurities in illuminating gas, an electric furnace giving the desired temperature was used. We soon found, however, that the platinum heat-producing resistance was volatilized to a serious extent. The fire-clay of the oven was soon partially coated by a black film of sublimed platinum, and an empty crucible heated in the oven for an hour gained 0.0002 gram. Qualitative analysis showed beyond doubt the nature of this sublimate, when deposited upon pure porcelain. This tendency of platinum under certain circumstances to volatilize has been studied by Hall;* it brought an unwelcome complication into the present work. Evidently platinum cannot safely be used as a resistance for obtaining high temperatures in accurate work; we had almost introduced a large error into the investigation while trying to eliminate a small one. Of course the temperature of the wire in the electric drying oven previously mentioned is too low to cause any danger from this source.

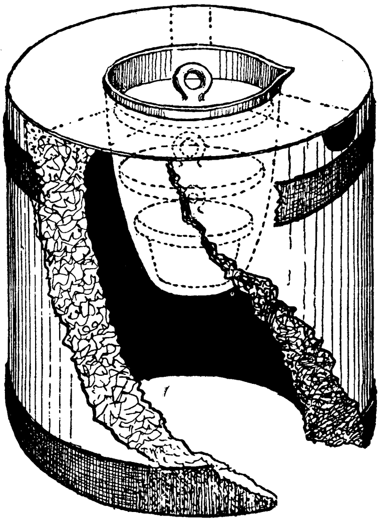

FIGURE 2.

Recourse was now had to a contrivance which had been used in this Laboratory in other work. Its general character will be seen from the diagram taken from the original paper. *

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* Hall, J. Am. Chem. Soc., **22**, 8, 494 (1900).

A large especially made crucible of Berlin porcelain fits tightly into a jacket or furnace of fire clay; the platinum crucible to be ignited is placed inside this, being protected from the porcelain by a spiral of platinum wire between the two crucibles. As a further protection from the impurities of the gas flame, the platinum crucible is fitted with a small porcelain cover, while a larger cover is placed above it. A circular opening is cut in two ignited asbestos sheets, lying on top of the furnace, into which the larger outside crucible fits tightly; these sheets serve as a further means of deflecting the impurities from the flame, since the only escape for the products of combustion is through the draught holes in the side. The asbestos sheets are not shown in the diagram. By means of this furnace the crucible can be heated at a uniform temperature for any length of time.

Experiments were made to ascertain if in this furnace any platinum volatilized from the crucible at high temperatures. When half full of silicic dioxide, no appreciable loss or gain was observed, either in the Bunsen flame or in the full flame of the blast lamp. When empty, however, although the crucible lost nothing in the Bunsen flame, it lost 0.00012 grams when heated for an hour in the blast. Evidently traces of platinum were volatilized from the *inside* of the vessel into the open air space. The outside annular space was probably kept saturated with platinum vapor from the platinum wire. Since the crucible was always more than half full of silica when placed in the furnace during the work described below, it was assumed that no platinum was lost by volatilization.

When the precautions indicated in this chapter are carefully followed no further complications arise, and the method easily yields constant results which seem to be unimpeachable.

The chief objections to the method lie in the fact that the nitrate must be wholly free from water (an end easily attained by gentle fusion in the present case †), and the further fact that any error which may occur is intensified in the calculation, as is always the case when the two substances weighed both contain either the element whose atomic weight is sought or the standard of reference.

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* Richards, Proc. Amer. Acad., **33**, 399 (1898); Am. Chem. J., **20**, 701 (1896).

† Stas (Aronstein), Untersuchungen, 235 (1867).

VI. THE ANALYSIS OF POTASSIC NITRATE.

The details of experimentation having been mastered, three careful analyses of potassic nitrate were made.

The salt lends itself easily to purification by recrystallization, on account of the great temperature coefficient of its solubility; it was recrystallized eight times in Jena glass vessels and four more times in platinum. The product thus obtained was carefully dried and fused in a platinum dish at the lowest temperature possible, in order to avoid the formation of even a trace of nitrite. The pure white solid was finely powdered and again dried. Although, as Hempel has shown,* a hard mineral causes considerable abrasion in an agate mortar, a soft substance like potassic nitrate may be powdered safely in one.

In every case at least five times as much of the silica by weight was used as of the nitrate.

In order to reduce the observed weights to the vacuum standard, the specific gravity of the potassic nitrate was taken as 2.09.† It was assumed that the contraction which takes place when potassic oxide combines with silica is negligible as far as the reduction to vacuum is concerned, and hence that the specific gravity of potassic oxide may be taken as 2.65, according to Karsten.‡

Following are the results of the three consecutive determinations of the atomic weight of potassium, using the nitrate prepared in the manner described above.

RESULTS OF ANALYSIS OF POTASSIC NITRATE.

$O = 16.000$; $N = 14.040$.

No. of Analysis.	Weight of N_2O_5 in Vacuum.	Weight of KNO_3 in Vacuum.	Ratio $N_2O_5 : K_2O = 100.00 : x$.	Atomic Weight of Potassium.
	grams.	grams.	$x =$	
30	0.96692	1.81034	87.227	39.138
31	1.68005	3.14564	87.235	39.142
32	1.36512	2.55598	87.235	39.142
		Average	87.232	39.141

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* Hempel, Chem. Centralbl., **2**, 719 (1901).

† Landolt and Börnstein, Tabellen (1894), 134. This is the most probable average of many determinations.

‡ Karsten, Schweigger's Ann., **65**, 419 (1832).

The average of these results (39.141) agrees well with that obtained from the chloride (39.139), and the constancy of the results indicates that the method is adequate for its purpose.

VII. The Analysis of Caesic Nitrate.

The decomposition of caesic nitrate may be effected in precisely the same fashion as that of potassic nitrate. The only points to be considered especially are the preparation of the pure salt and the data necessary for reduction to the vacuum standard.

Very pure caesic nitrate prepared from the four times recrystallized dichloriodide, and subsequently twice recrystallized, had already been prepared for us by Professor Wells. Like potassic nitrate, it is very easy to recrystallize.*

After gentle fusion this preparation was finely powdered, and served for the first two analyses. In order to test its purity, a portion was twice recrystallized in platinum vessels, very carefully fused in platinum, powdered as before, and subjected to analysis. Because the results were identical with those obtained from the first sample, further purification seemed unnecessary.

No measurements of the specific gravity of caesic nitrate could be found, therefore this constant was determined, since its value is needed in order to find the weight of air displaced. 1.7638 grams of fused caesic nitrate displaced upon one occasion 0.4210 gram and at another time 0.4208 gram of rectified benzol at 28° C. The specific gravity of the benzol was 0.880, 20°/4° ; therefore the specific gravity of the caesic nitrate must be 3.687.

In determining the air displaced by caesic oxide when combined with silica, the only fact available is the density of the hydrate. If we assume that the same contraction takes place when caesic oxide combines with water as when it combines with silica, the specific gravity of caesic oxide under these conditions is easily computed to be 4.9 if caesic hydroxide has a specific gravity 4.0,† as follows. Twice the molar volume of caesic hydroxide is 57 c.c. greater than that of water, and if the molar weight of caesic oxide is divided by this difference, the result given above is obtained. This assumption would have given in the case of potassium about the same result as that used under that head; and while it is of course inexact, it will answer sufficiently well the present purpose. In applying the corresponding correction, it was subtracted from that computed for the nitrate, and the difference added to the final weighing, in order to determine the true loss of weight which corresponds to the nitric pentoxide.*

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* Wells, Am. J. Sci., **3**, 46, 186.

† Békétoff, Bull. Acad. St. Petersb., **2**, 171 (1890); Ch. Centralbl., **2**, 451 (1891).

RESULTS OF THE ANALYSIS OF CAESIC NITRATE.

$O = 16.000$; $N = 14.040$.

No. of Analysis.	Sample of $CsNO_3$.	Weight of N_2O_5 in Vacuum.	Weight of $CsNO_3$ in Vacuum.	Ratio $N_2O_5 : Cs_2O = 100.000 : x$.	Atomic Weight of Caesium.
		grams.	grams.		
33	I	1.04273	3.76112	260.699	132.882
34	I	0.92416	3.33334	260.689	132.876
35	II	1.33590	4.81867	260.706	132.886
36	II	1.39960	5.04807	260.679	132.871
		Average		260.693	132.879

In this case, as in all the other cases treated in this paper, the analyses were consecutive, and the table contains all that were made excepting such as were intentionally of a preliminary nature and not worthy of detailed mention. The results will be discussed in connection with the other data at the close of the paper.

VIII. THE ANALYSIS OF CAESIC BROMIDE.

While the preceding results seemed to be conclusive as to the atomic weight of caesium, it was thought desirable to study the bromide also, because this salt is capable of especially exact analysis.

The bromide is easily prepared. In the first place, by adding to the nitrate an excess of hydrobromic acid and bromine, the tribromide is obtained on cooling in the form of deep orange crystals. Pure materials, prepared by the well known methods of Stas, were used in this process. After having been freed from chlorine and iodine the bromine was redistilled five times; and the hydrobromic acid made from it was thoroughly washed in the gaseous state as well as twice distilled in aqueous solution, rejecting the first and last portions. Hence there is no possibility that the product could have contained either chlorine or iodine. The trace of mother liquor included in the crystals of tribromide was eliminated by means of several successive recrystallizations and washings with hydrobromic acid. After drying the crystals as thoroughly as possible in a centrifugal machine, they were placed in a porcelain dish and kept at a temperature of 80° C. in an electric drying oven until all obvious signs of the extra bromine had disappeared. The pure white bromide was then heated for eight hours at 150°, and subsequently dissolved in a little water and precipitated by means of pure concentrated hydrobromic acid. The crystals were provisionally dried over potash and were then ready to fuse. Like the chloride, they were not deliquescent in the ordinary air of the laboratory.

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* Let a = weight of nitrate in air, and m = its correction to the vacuum standard; b = the weight of the oxide in air, and n = its correction to the vacuum standard; c = weight of silica. Then the weight of nitric peroxide in vacuum = true loss of weight $= (a + c) + m - [(b + c) + n] = (a - b) + (m - n)$.

The apparatus for fusing, bottling, and weighing the bromide was similar to that used in the case of the chloride, except that an addition was provided for the sake of introducing a slight amount of perfectly dry hydrogen bromide into the nitrogen during the fusion. * This was done because the loss of a trace of bromine was feared, although indeed none was ever noticed. After partial cooling the acid was wholly replaced by pure dry nitrogen and finally by air, which had passed through a freshly filled train of purifiers and freshly sublimed phosphoric oxide. The fused product, like the chloride, affected neither methyl orange nor phenol phthalein in the preliminary tests made to prove the normality of the salt. Caesic bromide fuses at a point somewhat above 600° C., although below the softening point of hard glass, but the exact point was not determined.

The analysis of the salt was less troublesome than the analysis of the chloride, because of the very meagre solubility of argentic bromide, which served as the means of precipitating the bromine. The silver used was from the same sample as that used in the case of the chloride, its weight was determined as before, and the very faint trace of bromide in the last pure wash-waters was estimated with the nephelometer as in the case of analyses 11, 12, and 13.

The specific gravity of caesic bromide was found by Setterberg † to be 4.37; in verification of this value the following determinations of this constant were made. At different times 0.9964 and 0.8456 gram of

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* Richards and Baxter, Proc. Am. Acad., **33**, 124 (1897).

† Oefvers. Stockh. Acad. Forh., **39**, No. 6, 23 (1882). We are indebted to Mr. F. R. Fraprie for this reference, which has been generally overlooked.

the salt displaced 0.2004 and 0.1699 gram of benzol respectively, therefore the two results (since the benzol had the specific gravity 0.880 referred to water at 4°) were 4.382 and 4.378 respectively, the mean value being 4.380. The temperature was 20°. This value was used in correcting the weight of caesic bromide to the vacuum standard.

COMPARISON OF CAESIC AND ARGENTIC BROMIDES.

Ag = 107.93; Br = 79.955.

No. of Analysis.	Weight of CsBr in Vacuum.	Weight of AgBr in Vacuum.	Atomic Weight of Cs.
	grams.	grams.	
37	3.49820	3.08815	132.878
38	6.20409	5.47673	132.883
39	7.17300	6.33213	132.880
		Mean =	132.880

COMPARISON OF CAESIC BROMIDE AND SILVER.

Ag = 107.93; Br = 79.955.

No. of Analysis.	Weight of CsBr in Vacuum.	Weight of Ag in Vacuum.	Atomic Weight of Caesium.
	grams.	grams.	
40	3.49820	1.77402	132.873
41	6.20409	3.14606	132.885
42	7.17300	3.63740	132.884
		Mean =	132.881

The agreement of these analyses with one another and with the previous results seems to indicate their trustworthiness. Further emphasis may be laid upon this consistency by pointing out that the 8.55748 grams of silver produced 14.8970 grams of argentic bromide, which must then have contained 57.444 per cent of silver. Stas found 57.445 per cent, or essentially the same value.

IX. THE ATOMIC WEIGHTS OF CAESIUM, POTASSIUM, AND NITROGEN.

In the preceding description are recorded analytical results involving the atomic weights of caesium, potassium, nitrogen, chlorine, bromine, silver, and oxygen. Of these, by common consent, the value for oxygen is fixed; the others may be calculated in many ways from the data in connection with the data obtained by other experimenters.

No attempt was made to explore any such complete experimental field as that suggested by Clarke[*] in his recent paper on the calculation of atomic weights. This omission was due not so much to lack of time as to the feeling that some of the results would have been fruitless. Experimental skill in attaining uniformity of conditions can almost always reduce the so called "probable error" of manipulation to a vanishingly small quantity; but constant errors of a chemical nature are much harder to avoid and much more serious when perpetrated. Hence the "probable error" is little or no clue to the trustworthiness of the results, and can rarely be used as a reliable measure of the relative preponderance to be ascribed to the respective members of a series of conflicting figures.[†] Instead of attempting to observe the weight of every element which combines with a given weight of every other without discrimination, it seems much wiser to select those operations in which the constant errors, by long and thorough study, have been discovered and rendered susceptible of elimination. A single series of experiments, and thoroughly investigated and properly executed, is of more value than ten series containing unknown and incorrigible errors.

The preceding figures involve seven different ratios for determining the atomic weight of caesium, assuming in each case one or more of the other atomic weights to be known. Five of these are obvious in the results given; the other two refer the salts of caesium to those of potassium. These latter ratios are of interest because they eliminate, at least in part, any possible constant errors in the processes immediately employed, by virtue of the parallelism between the experiments with the two metals. The atomic weight of caesium should therefore be influenced only by those constant errors which already affect the assumed atomic weight of potassium. 100.000 parts of silver were found to be equivalent to 155.964 and 69.115 parts of caesic and potassic chlorides respectively, hence these two weights must be equivalent to one another, or 100.000

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[*] Am. Chem. J., **27**, 321 (1902).

[†] Richards, A Table of Atomic Weights, Am. Chem. J., **20**, 543 (1898).

of potassic to 225.659 of caesic chloride. Again, 100.000 parts of argentic chloride were found to result from the precipitation of 117.398 and 52.022 parts of the same chlorides, a result which gives the almost equal ratio 100.000 : 225.670. The average of these two, 225.665, is given below.

In the same way, 100.000 parts of nitric anhydride were found to be equivalent to 87.232 and 260.693 parts of potassic and caesic oxides respectively.

A similar calculation might be performed with the bromide, using Stas's data obtained from potassic bromide; but this result would not have the same significance because the experimental work would not then have been done all by the same hands under the same conditions.

Below is given a table containing the results for the constant in question computed from the several ratios. After each standard substance is given its assumed molecular weight, and after each value of the atomic weight of caesium is given the "mean error" or average deviation from the mean. This is chosen rather than the "probable error" because the latter is in most cases too small to possess important significance. In the cases of the last two ratios the average of the mean errors of the potassium and caesium series is recorded.

From	AgCl	(143.385)	: CsCl,	Cs = 132.876	± 0.003
“	Ag	(107.93)	: CsCl,	Cs = 132.877	± 0.003
“	AgBr	(187.885)	: CsBr,	Cs = 132.880	± 0.002
“	Ag	(107.93)	: CsBr,	Cs = 132.881	± 0.004
“	N_2O_5	(108.08)	: Cs_2O,	Cs = 132.879	± 0.005
“	KCl	(74.595)*	: CsCl,	Cs = 132.879	± 0.002
“	K_2O	(94.280)	: Cs_2O	Cs = 132.879	± 0.003
	Average			132.879†	

It is of interest to note that not one of these seven independent figures deviates from the average of all by an amount greater than its mean experimental error. The inference to be drawn from this is that constant errors have been essentially eliminated from the various chemical processes involved.

For the atomic weight of potassium we have three direct ratios, which give the following results: —

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* This value of potassic chloride is known directly with reference to oxygen from the analysis of potassic chlorate, which (according to Clarke) contains 39.154 per cent of oxygen.

† If O = 15.879, Cs = 131.874.

$AgCl$ (143.385) : KCl gives $K = 39.137 \pm 0.001$
Ag (107.93) : KCl gives $K = 39.141 \pm 0.001$
N_2O_5 (108.08) : K_2O gives $K = 39.141 \pm 0.002$
Average 39.140

This result confirms the results of Stas, but disagrees with Clarke's value (39.11) by nearly one tenth of a per cent. The reason for the difference is to be traced chiefly to the influence of some relatively inexact analyses of potassic iodide by Marignac, which have seriously reduced Clarke's average value; moreover Clarke's estimate of chlorine is somewhat lower than ours. The value given above, 39.14, seems to us to represent more nearly the true atomic weight of potassium.

On the other hand, assuming from the experiments with the halides, that the atomic weights of caesium and potassium are respectively 132.879 and 39.139, it becomes possible to calculate the atomic weight of nitrogen from the analysis of the nitrate. Since the atomic weight sought is not included in both of the substances weighed, an error is not magnified by the calculation.

Cs_2O (281.758) : N_2O_5, $N = 14.040$
K_2O (94.278) : N_2O_5, $N = 14.037$
Average . . . $N = 14.039$

This value affords another confirmation of the remarkable work of Stas.

Many other combinations of the preceding data with those of other experimenters might have been made, but the preceding are enough to show the most important features of the new investigation.

It is a pleasure to acknowledge our indebtedness to the Cyrus M. Warren Fund for Research in Harvard University for some of our apparatus, and to Dr. Wolcott Gibbs for invaluable platinum utensils, as well as to Professor Wells for his great generosity in providing the caesium material.

X. SUMMARY.

1. As an outcome of forty-two analyses involving seven different ratios and three compounds of caesium (the chloride, bromide, and nitrate), the atomic weight of caesium is found to be 132.879, if oxygen is 16.000.

2. Incidentally it is found that the atomic weights of potassium and nitrogen most consistent with the new data are nearly 39.14 and 14.04.

3. In confirmation of Wells, caesium dichloriodide is found to afford

a convenient and exceptionally thorough means of purifying caesium material.

4. No evidence was found indicating the presence of any similar element of higher atomic weight, except a trace of thallium.

5. The specific gravities of caesic chloride, bromide, and nitrate were found to be respectively 3.972, 4.380, and 3.687; and the melting point of the nitrate was found to be 414° C.

6. The precautions necessary to effect the precisely quantitative decomposition of alkaline nitrates are described.

CAMBRIDGE, MASS.
October, 1900, to November, 1902.